



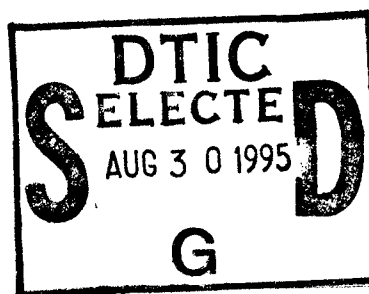
A COMPARISON OF THIN FILM SULFURIC ACID ANODIZING AND CHROMIC ACID ANODIZING PROCESSES

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April 25, 1995

FINAL REPORT

Approved for Public Release; Distribution unlimited

Prepared for
NAVAL AIR SYSTEMS COMMAND
Washington, DC 22202

19950828 053

DTIC QUALITY INSPECTED 8

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Reviewed By: Stephen J. Spadafora Date: 26 April 95
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Reviewed By: James J. Koffen Date: 6/6/95
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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 25 Apr 95	3. REPORT TYPE AND DATES COVERED (October 1993-April 1995)		
4. TITLE AND SUBTITLE A Comparison of Thin Film Sulfuric Acid Anodizing and Chromic Acid Anodizing processes		5. FUNDING NUMBERS Program 0603721N		
6. AUTHOR(S) Stephen M. Cohen Stephen J. Spadafora		Work Unit 100337		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Aerospace Materials Division Air Vehicle Technology Department NAVAL AIR WARFARE CENTER AIRCRAFT DIVISION P.O. Box 5152 Warminster, PA 18974-0591		8. PERFORMING ORGANIZATION REPORT NUMBER NAWCADWAR-95023 -43		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval Air Systems Command Washington, DC 20361-0001		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for Public Release; Distribution unlimited		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) Chromic acid anodizing (CAA), a common aluminum pretreatment, forms a thick oxide film which provides protection against environmental degradation. Chromium VI, however, is a carcinogen and its widespread use as a corrosion inhibitor is being restricted. The Navy has targeted chromated maintenance operations for reduction of hazardous waste generation. Alternative anodize processes include: Phosphoric Acid Anodizing, Boeing Aerospace Corp's Boric-Sulfuric Acid Anodize and thin film sulfuric acid anodizing (TFSAA). This report describes an investigation on the performance properties of TFSAA and CAA both sealed and unsealed on various substrates with and without standard Navy coating systems. At specific coating weights, TFSAA could effectively provide equivalent corrosion resistance and paint adhesion as compared to CAA. Replacement of CAA eliminates the need for expensive control equipment required under the Clean Air Act, resulting in \$M's in cost avoidance for the Navy.				
14. SUBJECT TERMS Inorganic Coatings Anodizing processes Non-Chromate Pretreatments			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT SAR	

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Introduction

Increasing concern over environmental quality has caused national and local legislatures to tighten controls over handling, use, and disposal of hazardous materials and wastes. According to the Department of Defense, the majority of hazardous waste and materials is generated within its maintenance depots and operations¹. These materials generally are derived from metal finishing processes such as cleaning, pretreating, plating, painting, and paint removal. One major contributor to such hazardous waste is chromium. The Environmental Protection Agency has issued a national emission standard for hazardous air pollutants (NESHAP) on the emissions from electrolytic chromium processes², similar to California's South Coast Air Quality Management District Rule 1169.

Naval aircraft, weapons platforms, and ground support equipment currently use chromic-acid anodizing as a surface pretreatment for aluminum. This anodization technique provides more protection against degradation than chemical conversion coatings, via its thick oxide film. The performance requirements for chromic-acid anodizing are listed in military specification MIL-A-8625F, "Anodic Coatings for Aluminum and Al Alloys," Type I and IB. Despite the acceptable performance of chromic-acid anodizing, elimination of chromium emissions will be required in the future.

Two possible solutions to eliminate chromium are available. One method requires use of process emission controls. The other directly eliminates the hazardous source by substituting either non-hazardous materials or alternative technologies. This second approach also solves disposal and handling problems. Elimination of chromic-acid anodizing will reduce significantly the total amount of chromium derived from Naval operations, and directly supports the hazardous waste minimization directives promulgated by the Navy and Department of Defense. With chromium eliminated, there would be no need for expensive control equipment as required by the NESHAP. Initial estimates for control equipment for Naval depots were around \$0.5–1 million for capital costs and \$250K–400K for annual operating costs per facility. Furthermore, adequate replacements need to protect against excessive environmental degradation. Considering the particularly harsh environment for Naval operations, and high equipment costs of aircraft, weapons systems, and support equipment, finding chromium replacements is particularly important.³

The Naval Air Warfare Center, Aircraft Division, at Warminster, has a diverse environmental materials program aimed at the removal of hazardous materials from Naval aerospace processes.⁴ Previous efforts under this program have resulted in the approval of sulfuric-acid/boric-acid anodizing as a substitute for chromic-acid anodizing.⁵ A second non-chromated alternative is thin-film sulfuric-acid anodizing (Type IIB in specification MIL-A-8625F).^{6,7,8,9} This report summarizes the results from a study of the performance properties of this alternative process.

Procedures

Surface Preparation

Two aluminum alloys, 7075-T6 and 2024-T3, 1/32" thick and cut into 3"×10" panels, were used for this investigation. Prior to anodization, several steps were followed to prepare the surface: cleaning, etching, and deoxidizing. In order to remove organic contaminants and surface oxides before anodization, non-chromated solutions were used for all three steps. The materials used (Turco 4215-NC-LT and Smut-Go-NCB) were non-silicated, non-chromated solutions described elsewhere.¹⁰

Thin-Film Sulfuric-Acid Anodizing Process

The anodizing bath was five percent H₂SO₄ by volume. The anodizing voltage used was 15 V for 7075 and 17.5 V for 2024, and was reached by ramping up from zero at 2 V min⁻¹. To test the effects of anodic oxide thickness, two different coating weights were analyzed for each alloy. Unpainted thin-film sulfuric-acid anodized panels were sealed for 25 min in a dilute dichromate solution. For certain tests, including a detailed examination of the effects of coating weight, thin-film sulfuric-acid anodized panels were sealed for 5 to 10 min in deionized hot (95 °C) water. For comparative purposes, a standard chromic-acid anodizing bath was also used, with anodizing voltages of 20 V for 7075 alloy and 40 V for 2024 alloy.^{11,12} Chromic-acid anodized panels were sealed in hot water. For both anodization processes, painted panels were not sealed prior to painting, although a few panels (noted in the text) were sealed in hot water.

Coating Weight Determination

Coating weights were chemically determined according to MIL-A-8625F, and film thickness were measured by a Permascope eddy-current thickness gauge. Because a linear correlation was found dependent upon alloy and anodizing process, as shown in Figure 1, all further coating weights were determined solely via Permascope measurements. Anodized films were divided into low (400–600 mg ft⁻²) and high (800–1000 mg ft⁻²) coating weights for the thin-film sulfuric-acid anodization process, and 450–600 mg ft⁻² for chromic-acid anodizing, as shown in Table 1.

Table 1. Coating Weights for Test Program (mg-ft⁻²)

Alloy	Low Weight Thin-Film H ₂ SO ₄	High Weight Thin-Film H ₂ SO ₄	Chromic-Acid
7075-T6	562.1	823.0	570.3
2024-T3	412.0	852.3	497.8

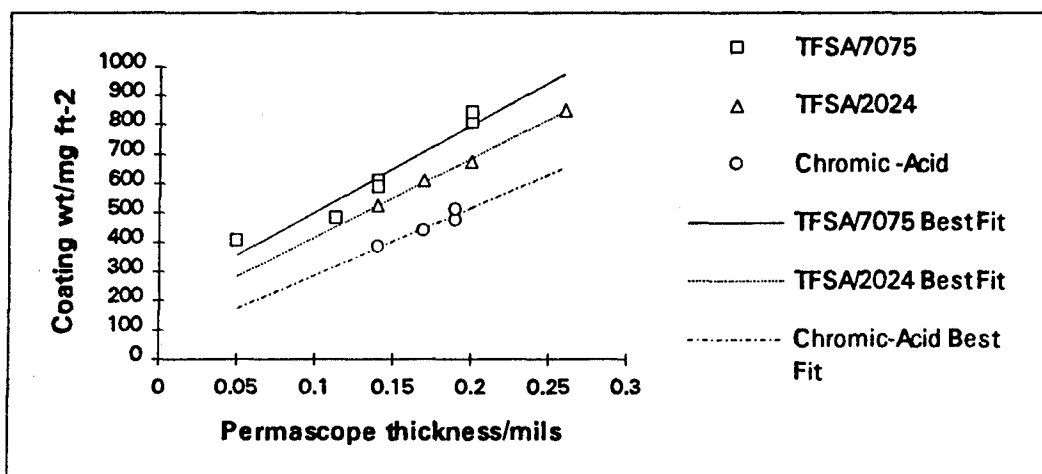


Figure 1. Permascope thickness d vs coating weight for pretreatments on various alloys. Best fit equations are TFSA/7075 = $2944.5 d + 209.47$ ($r = 0.970$); TFSA/2024 = $2678.1 d + 150.47$ ($r = 0.998$); Chromic-acid = $2288.1 d + 60.060$ ($r = 0.965$). TFSA/xxxx is thin-film sulfuric-acid on alloy xxxx.

Paint Systems

To determine adhesion, water resistance, and corrosion properties of organic coatings, the following paints were applied to some of the panels: MIL-P-23377 epoxy primer, MIL-P-85582 epoxy waterborne primer, and TT-P-2760 elastomeric polyurethane primer.^{13,14,15,16} To determine the effects of primed and topcoated samples, some coupons painted with MIL-P-23377 primer were then topcoated with MIL-C-85285 high-solids polyurethane. Table 2 shows the appropriate specifications and film thicknesses for each coating applied. All coatings were applied via conventional air spray, and were allowed to cure for 14 days before testing.

Table 2. Specifications for Organic Coatings

Coating	Title	Thickness
MIL-P-23377D, Type 1	Primer Coatings: Epoxy Polyamide, Chemical and Solvent Resistant	15.2–22.9 μm (0.0006–0.0009")
MIL-P-85582A, Type 1	Primer Coatings: Epoxy, Waterborne	15.2–22.9 μm (0.0006–0.0009")
TT-P-2760, Type 1	Primer Coatings: Polyurethane, Elastomeric	20.3–30.5 μm (0.0008–0.0012")
MIL-P-23377D, Type 1 + MIL-C-85285B, Type 1	Primer Coatings: Epoxy Polyamide, Chemical and Solvent Resistant; Coating: Polyurethane, High Solids	15.2–22.9 μm (0.0006–0.0009"); 45.7–55.9 μm (0.0018–0.0022")

Results

Adhesion/Water Resistance

To evaluate the adhesion of organic coating systems to the anodized films, two methods were employed. Dry scrape results, performed in accordance with American Society for Testing and Materials ASTM D 2197 (method A), are shown in Table 3. The apparatus and detailed method are listed elsewhere.⁵ Results varied widely, from 1 to 8.5 kg, for the thin-film sulfuric-acid process, comparable to 1.5 to >10 kg for the chromic-acid process. Dry tape adhesion tests gave nearly all 5A ratings for all paint systems tested as shown in Table 3. The standard rating scheme for this test is listed in Table 4.

Table 3. Dry Scrape and Tape-Adhesion, and Humidity Chamber Results

Alloy/Coating	Low Weight Thin-Film H ₂ SO ₄			High Weight Thin-Film H ₂ SO ₄			Chromic-Acid		
	Scrape /kg	Dry Tape	Humi- dity	Scrape /kg	Dry Tape	Humi- dity	Scrape /kg	Dry Tape	Humi- dity
7075-T6									
MIL-P-23377D	1	5A	P	1.5	5A	P	1.5	5A	P
MIL-P-85582A	3	5A	P	3.5	5A	P	5.5	5A	P
TT-P-2760	5	5A	P	6	5A	P	4	5A	P
23377D + MIL-C-85285B	4.5	4A	F	8.5	5A	P	10	5A	P
2024-T3									
MIL-P-23377D	1.5	5A	P	4	5A	P	> 10	5A	P
MIL-P-85582A	3.5	5A	P	5	5A	P	3	5A	P
TT-P-2760	6	5A	P	7.5	5A	P	4.5	5A	P
23377D + MIL-C-85285B	5.5	5A	P	5	5A	P	6	5A	P

Wet tape adhesion, as described in ASTM D 3359 and elsewhere⁵, was also used. Results are provided in Table 5. For chromic-acid anodizing, all wet-tape adhesion tests gave 4A or 5A ratings. On thin-film sulfuric-acid films, 24 h wet-tape-adhesion results gave 4A or 5A ratings for 85582 (waterborne) and 2760 (polyurethane) primers, but 0A or 1A ratings for 23377 (epoxy) primer alone or in combination with 85285 topcoat. After four days, tape-adhesion markedly improved to 4A or 5A ratings on all systems except primed and topcoated 7075 alloy, which gave a 0A or 1A. Nearly all paint systems gave 5A ratings after 7-day tape-adhesion tests. One possible explanation for this increase in performance may be associated with cure state. The panels tested may not have been fully cured, so that exposure at the elevated temperatures actually may have cured the coating further, resulting in a better performance rating.

Humidity resistance results, following storage of panels in a cabinet containing 100% relative humidity at 120 °F for 30 d, are provided in Table 3. All panels passed this test, producing no

Table 4. ASTM D 3359 Rating Scheme for Adhesion

Rating	Description
5A	No peeling or removal of paint
4A	Trace peeling or removal along incisions
3A	Jagged removal along incisions up to 1/16" (1.6 mm) on either side
2A	Jagged removal along most of incisions up to 1/8" (3.2 mm) on either side
1A	Removal from most of the area of the X under the tape
0A	Removal of paint beyond the area of the X

Table 5. Wet-Tape Adhesion Results

Alloy/Coating	Low Weight Thin-Film H ₂ SO ₄			High Weight Thin-Film H ₂ SO ₄			Chromic-Acid		
	Wet Tape (1 d)	Wet Tape (4 d)	Wet Tape (7 d)	Wet Tape (1 d)	Wet Tape (4 d)	Wet Tape (7 d)	Wet Tape (1 d)	Wet Tape (4 d)	Wet Tape (7 d)
7075-T6									
MIL-P-23377D	0A*	4A*	5A*	0A	4A	5A	5A	5A	5A
MIL-P-85582A	5A	5A	5A	5A	5A	5A	5A	5A	5A
TT-P-2760	4A	4A	5A	5A	5A	4A	5A	5A	5A
23377D + MIL-C-85285B	1A	1A	5A	1A	4A	5A	5A	5A	4A
2024-T3									
MIL-P-23377D	0A	4A	4A	0A	4A	5A	5A	5A	5A
MIL-P-85582A	5A	5A	5A	5A	5A	5A	5A	5A	5A
TT-P-2760	4A	4A	5A	4A	4A	5A	5A	5A	5A
23377D + MIL-C-85285B	1A	4A	5A	1A	4A	5A	5A	5A	5A

*These received "5A" ratings when sealed in hot water before priming.

delamination or blistering, except low-coating-weight thin-film sulfuric-acid anodized 7075 panels, on which a few blisters were observed.

Water-immersion tests (Table 6) to an extent mirrored the tape-adhesion results: For chromic-acid anodizing, all panels passed all tests. On thin-film sulfuric-acid films, all 2024 alloy panels and those 7075 panels with high coating weights passed all tests. The 7075 panels with low coating weights painted with 23377 alone or topcoated had poor blistering resistance. When 7075 panels with low coating weights were sealed in hot water and then primed, however, they passed both water resistance and tape-adhesion (Table 5) tests.

Table 6. Water-Resistance Results

Alloy/Coating	Low Weight Thin-Film H ₂ SO ₄			High Weight Thin-Film H ₂ SO ₄			Chromic-Acid		
	Water Resis. (1 d)	Water Resis. (4 d)	Water Resis. (7 d)	Water Resis. (1 d)	Water Resis. (4 d)	Water Resis. (7 d)	Water Resis. (1 d)	Water Resis. (4 d)	Water Resis. (7 d)
7075-T6									
MIL-P-23377D	P*	P*	P*	P	P	P	P	P	P
MIL-P-85582A	P	P	P	P	P	P	P	P	P
TT-P-2760	P	P	P	P	P	P	P	P	P
23377D + MIL-C-85285B	F	F	F	P	P	P	P	P	P
2024-T3									
MIL-P-23377D	P	P	P	P	P	P	P	P	P
MIL-P-85582A	P	P	P	P	P	P	P	P	P
TT-P-2760	P	P	P	P	P	P	P	P	P
23377D + MIL-C-85285B	P	P	P	P	P	P	P	P	P

*These also passed when sealed in hot water before priming.

To determine the minimum coating weight that passes the water immersion test, a series of thin-film sulfuric-acid anodized coating weights ranging from 460 to 963 mg ft⁻² were processed on alloy 7075, primed, and subjected to this test. As shown in Table 7, below 600 mg ft⁻², poor tape adhesion was observed after 1 day in water at room temperature, while panels with coating weights above 600 mg ft⁻² passed. Some improvement was observed (rating 3A) after 4 days in water at 49 °C, while after 7 days in water at 65 °C all panels passed. All these panels gave acceptable water resistance at 1, 4, and 7 days.

**Table 7. Various Coating Weights on Bare, Sealed 7075 Alloy
Subjected to Immersion Tests**

Test Performed	Thin-Film H ₂ SO ₄ Anodized Coating Weight/mg ft ⁻²							
	460	504	575	648	694	760	787	963
Wet Tape (1 d)	0A	0A	1A	5A	5A	4A	5A	5A
Wet Tape (4 d)	3A	3A	5A	5A	5A	5A	5A	5A
Wet Tape (7 d)	5A	5A	5A	5A	5A	5A	5A	5A
Water Resistance (1-7 d)	P	P	P	P	P	P	P	P

Bare Corrosion Resistance

All panels passed 336 h of neutral salt-spray exposure. Panels were exposed till failure, and results are shown in Figure 2: The longest-lasting was thin-film sulfuric-acid on 7075; slightly worse was chromic-acid anodization; much worse was thin-film sulfuric-acid on 2024. Panels were also exposed to SO₂/salt spray (see Figure 3), with the following results: chromic-acid anodized panels lasted longest, for 168 h, while the thin-film sulfuric-acid panels corroded in a substantially shorter time.

Painted Corrosion Resistance

In neutral salt-fog, as shown in Figures 4 and 5, all paint systems lasted the required 2000 h. Because the result for 85582 was similar to 23377, and the combination of 23377 + 85285 was similar to 2760, these two graphs are not shown. Immediately after passing the 2000-h point, significant degradation in the scribe area was evident in those specimens painted with elastomeric polyurethane primer (2760), and the primed-and-top-coated (23377 + 85285) samples. Those panels coated only with primers 23377 or 85582 showed practically no degradation, even after 4500 h. For the four coating systems used, none of the panels failed after 4500 h. Figures 4 and 5 also show that panel performance is independent of pretreatment: both thin-film sulfuric- and chromic-acid anodized samples degraded equally rapidly. The rating system for the graph is based on 3 equaling a pass, 2 equaling a borderline pass, 1 equaling a borderline failure and 0 equaling a failure.

In SO₂/salt spray, ratings again are largely dependent on paint scheme, and less on underlying pretreatment or alloy. Primed and topcoated panels lasted longest (Figure 6), while those painted with 2760 were nearly equivalent. Those painted with 23377 primer alone performed moderately, while the 85582 primer was by far the worst for protection (Figure 7). Slight variations in performance can be observed among the various pretreatments and alloys. Figure 6 shows that both chromic-acid anodized alloys last somewhat longer when primed and topcoated, while chromic-acid anodized 2024 seems to last slightly longer when painted with 85582 primer in Figure 7. All specimens, however, passed at 168 h exposure, except for panels primed (but not topcoated) with 23377 on thin-film H₂SO₄ anodized 7075.

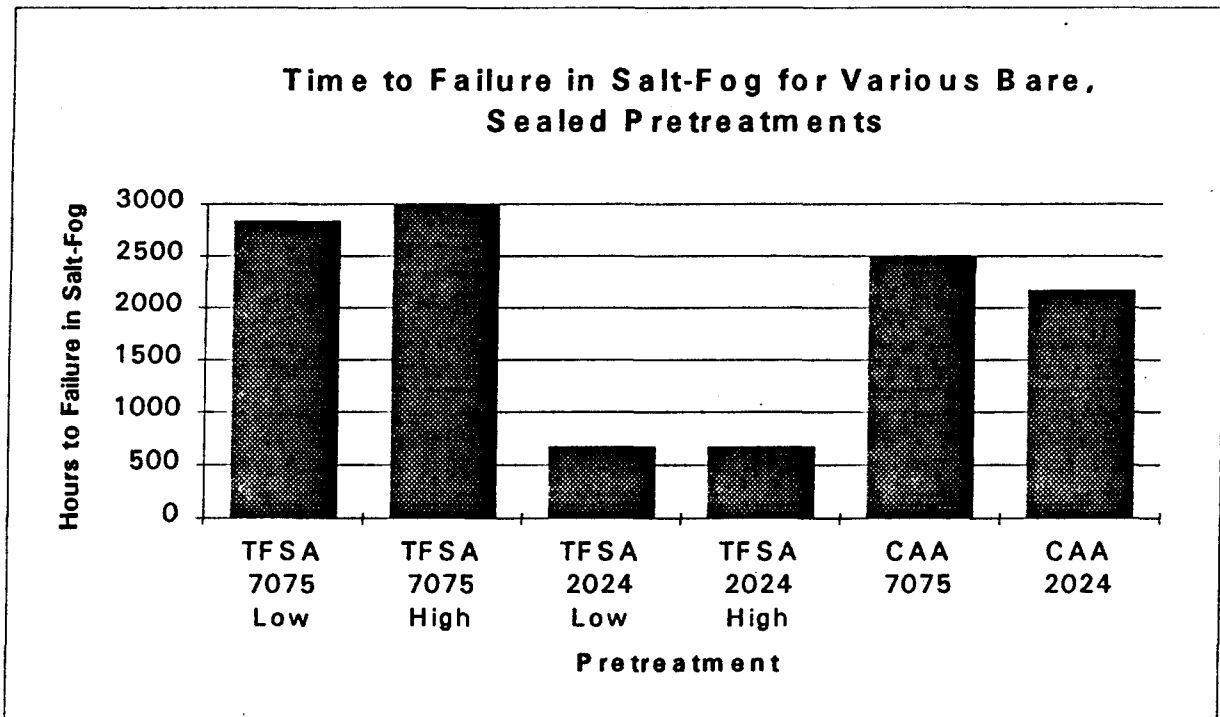


Figure 2. TFSA = Thin-Film Sulfuric-Acid Anodized; CAA = Chromic-Acid Anodized.

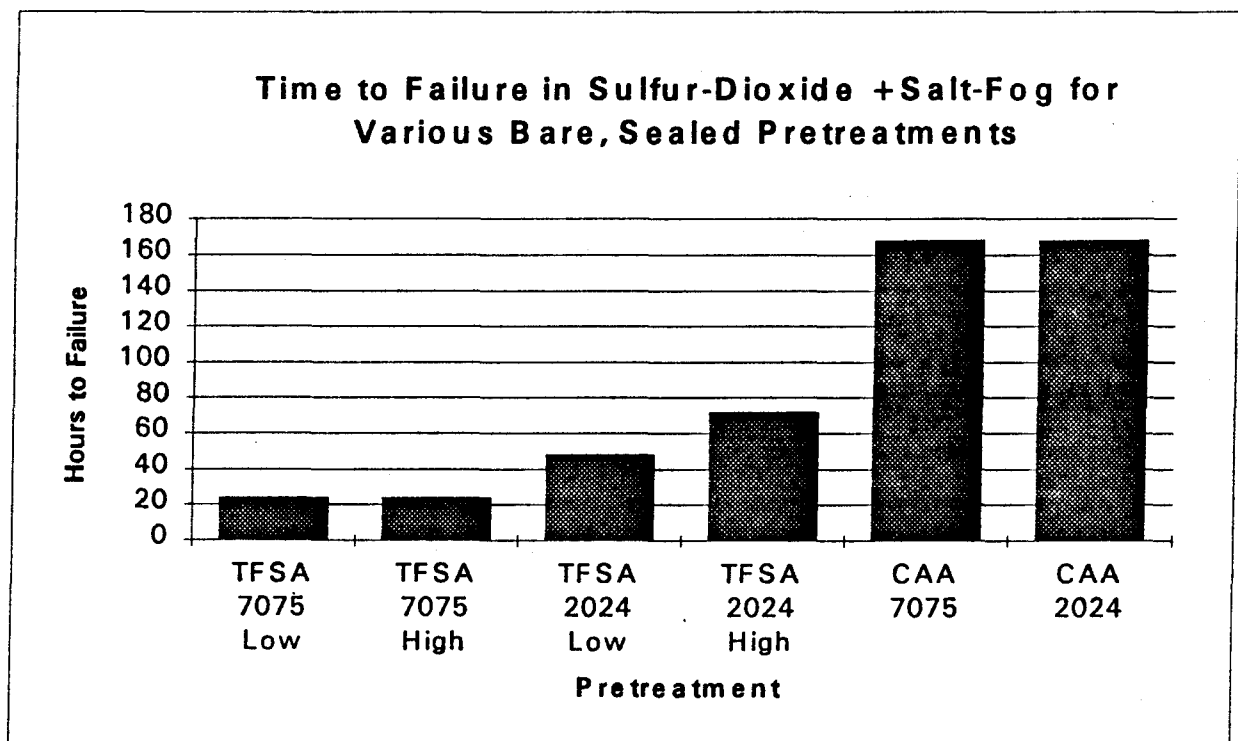


Figure 3. TFSA = Thin-Film Sulfuric-Acid Anodized; CAA = Chromic-Acid Anodized.

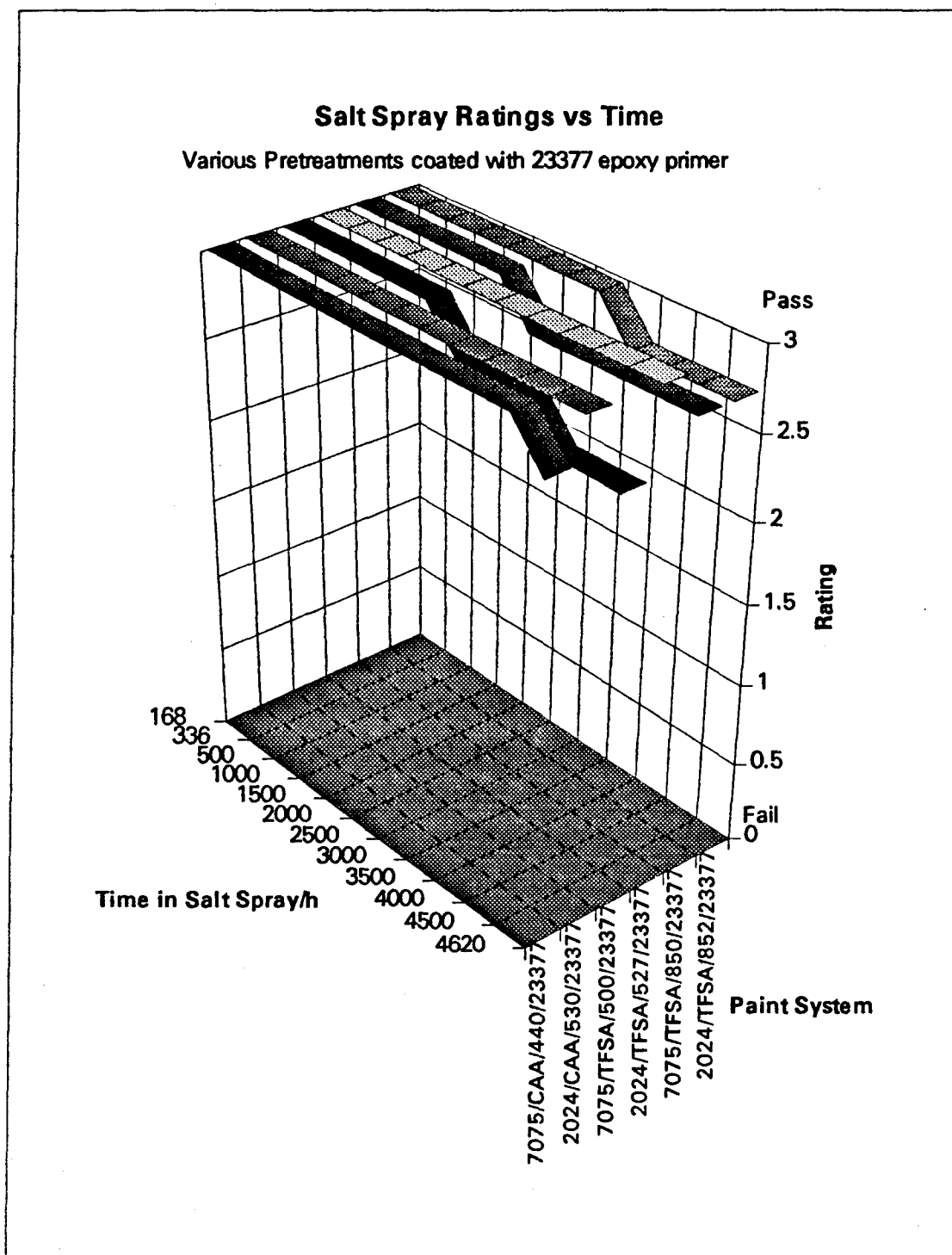


Figure 4. Paint system designation is alloy/pretreatment/coating weight (mg ft⁻²) /organic coating. TFSA = thin-film sulfuric-acid, CAA = chromic acid.

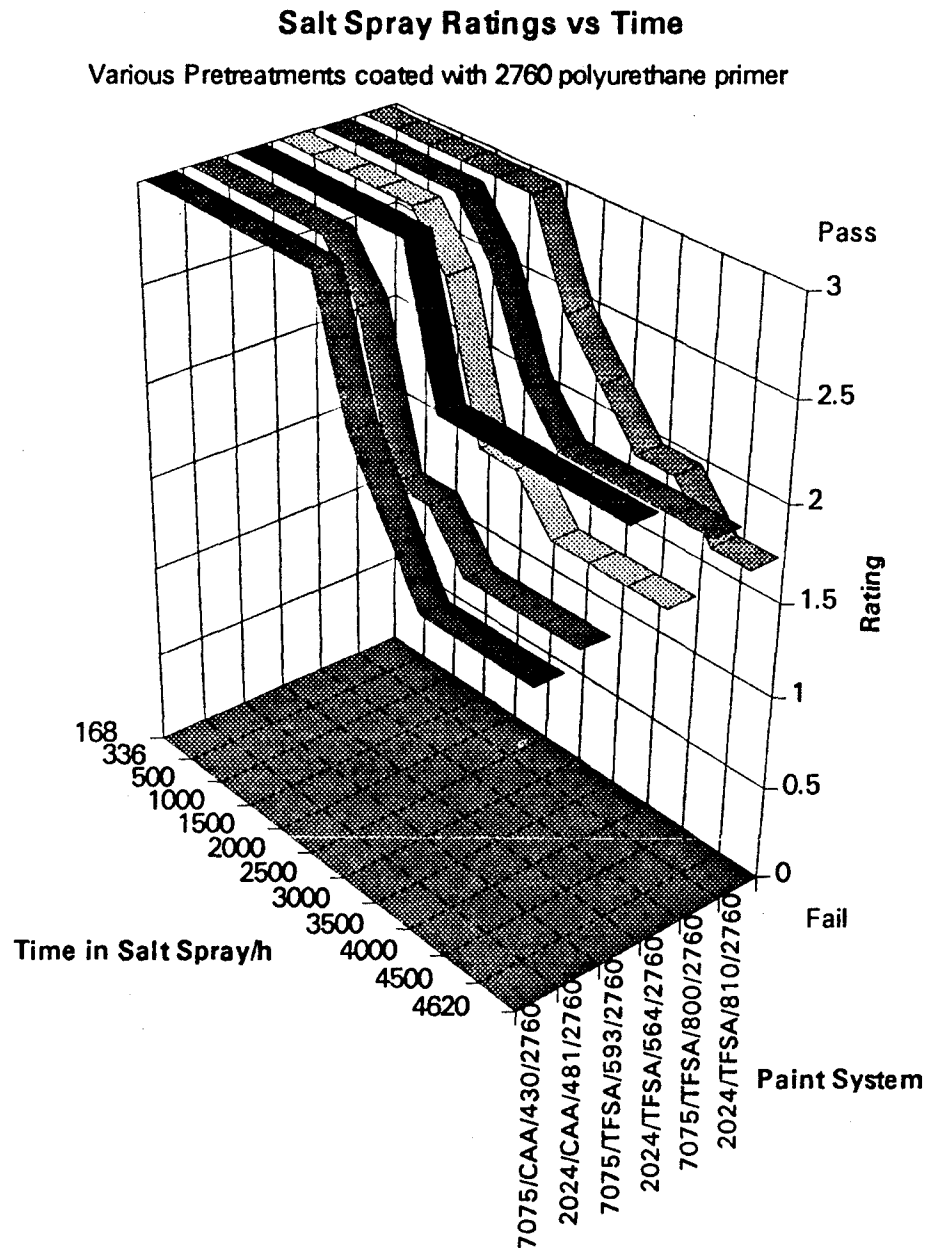


Figure 5. Paint system designation is alloy/pretreatment/coating weight (mg ft^{-2}) /organic coating. TFSA = thin-film sulfuric-acid, CAA = chromic acid.

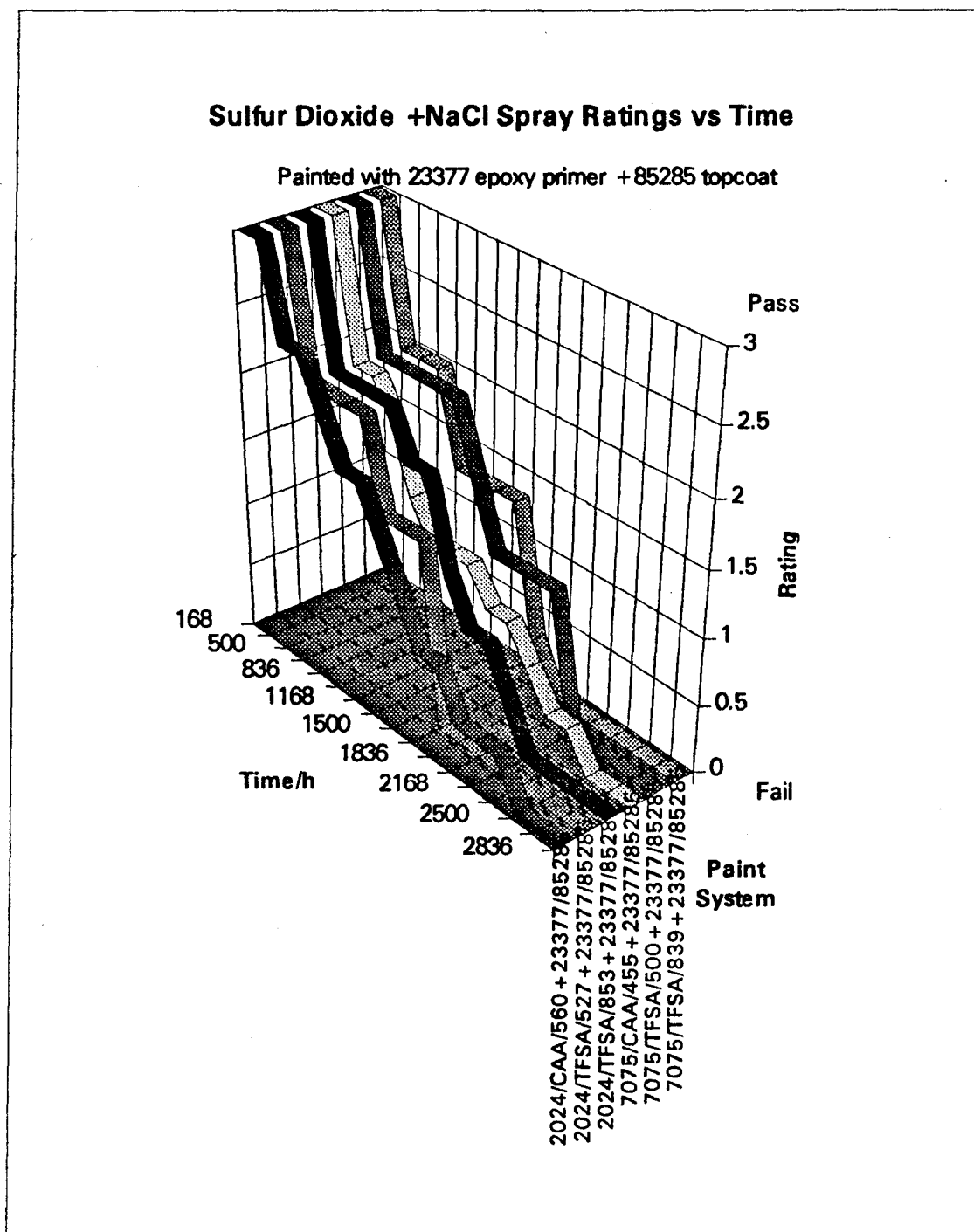


Figure 6. Paint system designation is alloy/pretreatment/coating weight (mg ft⁻²) /organic coating. TFSA = thin-film sulfuric-acid, CAA = chromic acid.

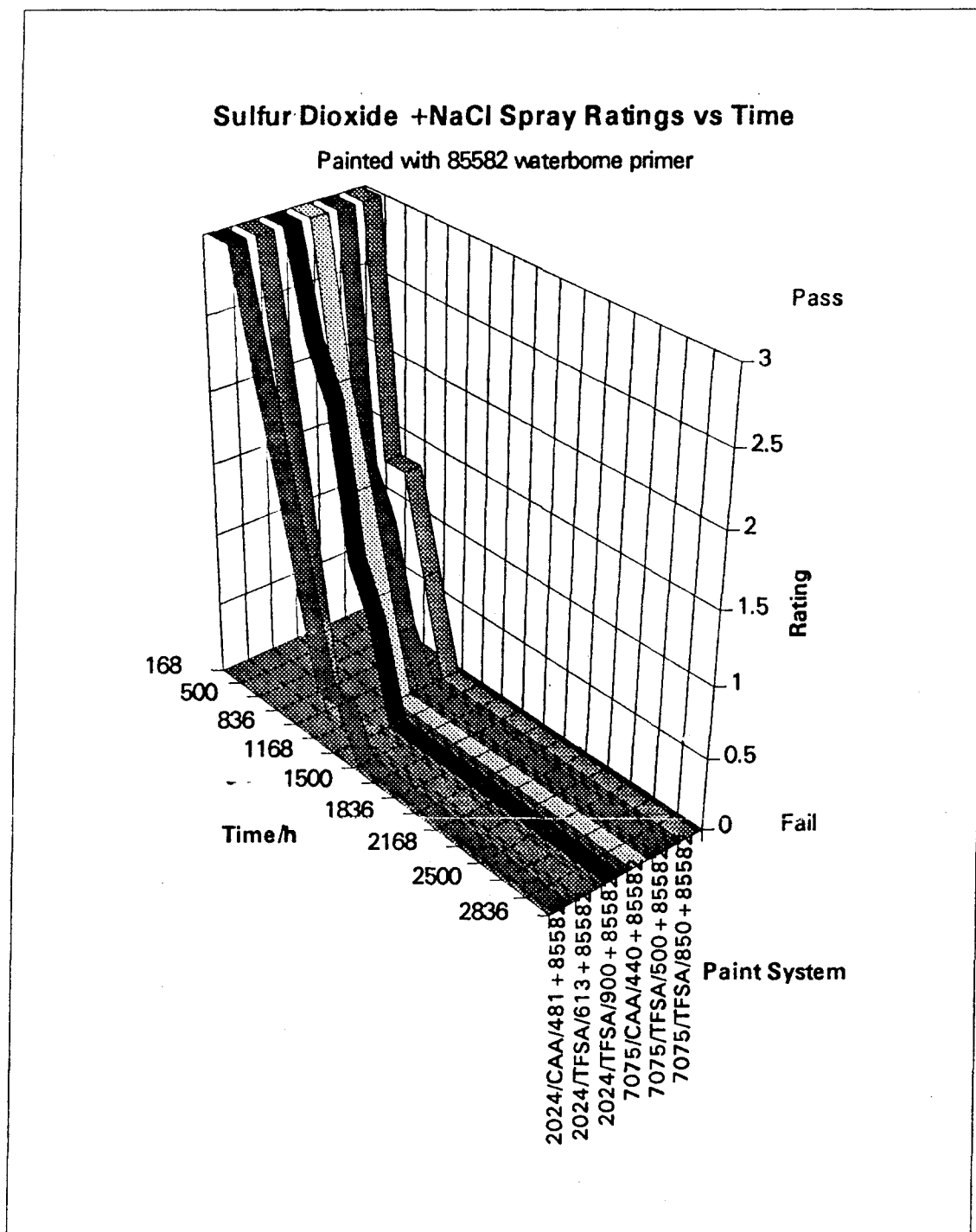


Figure 7. Paint system designation is alloy/pretreatment/coating weight (mg ft^{-2}) /organic coating. TFSA = thin-film sulfuric-acid, CAA = chromic acid.

EIS Results

General Procedure

In order to determine electrical characteristics, and thus indirectly, the microstructure, of the bare and painted panels, electrochemical impedance spectroscopy (EIS) was performed. All EIS measurements were made using a Princeton Applied Research potentiostat 273A and Schlumberger SI 1255 frequency response analyzer linked to an IBM PS/2 model 70 personal computer. A pyrex cell with 7.5 cm² surface area and a 3.5% NaCl solution were also used for this testing. Frequencies measured ranged from 0.01 Hz to 100 kHz at a superimposed amplitude of 5 mV. For painted panels, only those coated with MIL-P-23377 solvent-borne epoxy primer were analyzed. Model equivalent circuits were fit to the EIS data using Boukamp's EQUIVCRT non-linear-least-squares fitting program¹⁷ (version 4.51). In most cases where the impedance of the EIS circuit was less than ~100 Ω·cm² at applied frequencies > 10⁴ Hz, an instrument-dependent inductance (typically several μH) was required in series with the circuit.

Results for Bare, Sealed Panels

To model the bilayer structure of the bare, sealed panels, a standard dual-time-constant equivalent circuit was used consisting of: a solution resistance R_{sol} in series with a porous layer (R_p in parallel with constant-phase element Q_p), in series with a barrier layer (R_b in parallel with Q_b), as shown in Figure 8. In most cases, one or even two additional (RQ) terms were required to provide a good fit to the data.

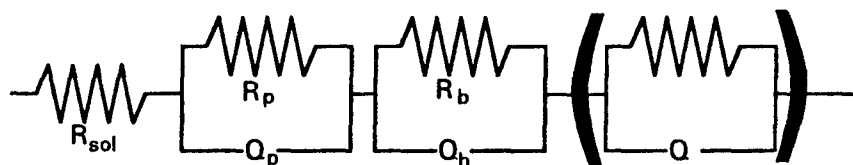


Figure 8. Equivalent circuit model for bare, sealed panels.

A constant-phase element Q may be regarded as an "imperfect" capacitor C (where surface inhomogeneities cause departure from perfect parallel plates), according to the relation

$$Q = C^n \quad (1)$$

When the exponent $n = 1$, Q is a perfect capacitor, but when n declines to about 0.5, chemical diffusion within the dielectric becomes important. Figures 9–11 show Bode plots for the different pretreatments on bare, sealed panels, at selected times during immersion under electrolyte. Bode plots for Al 2024 are not presented because they have strong similarities to those for Al 7075: low coating-weight thin-film H₂SO₄ on Al 2024 is similar to Fig. 10, high coating-weight thin-film H₂SO₄ on Al 2024 is similar to Fig. 9, and chromic-acid on Al 2024 is similar to Fig. 11. Table 8 compares circuit values derived from the spectra taken from bare, sealed panels after only 1 day under electrolyte.

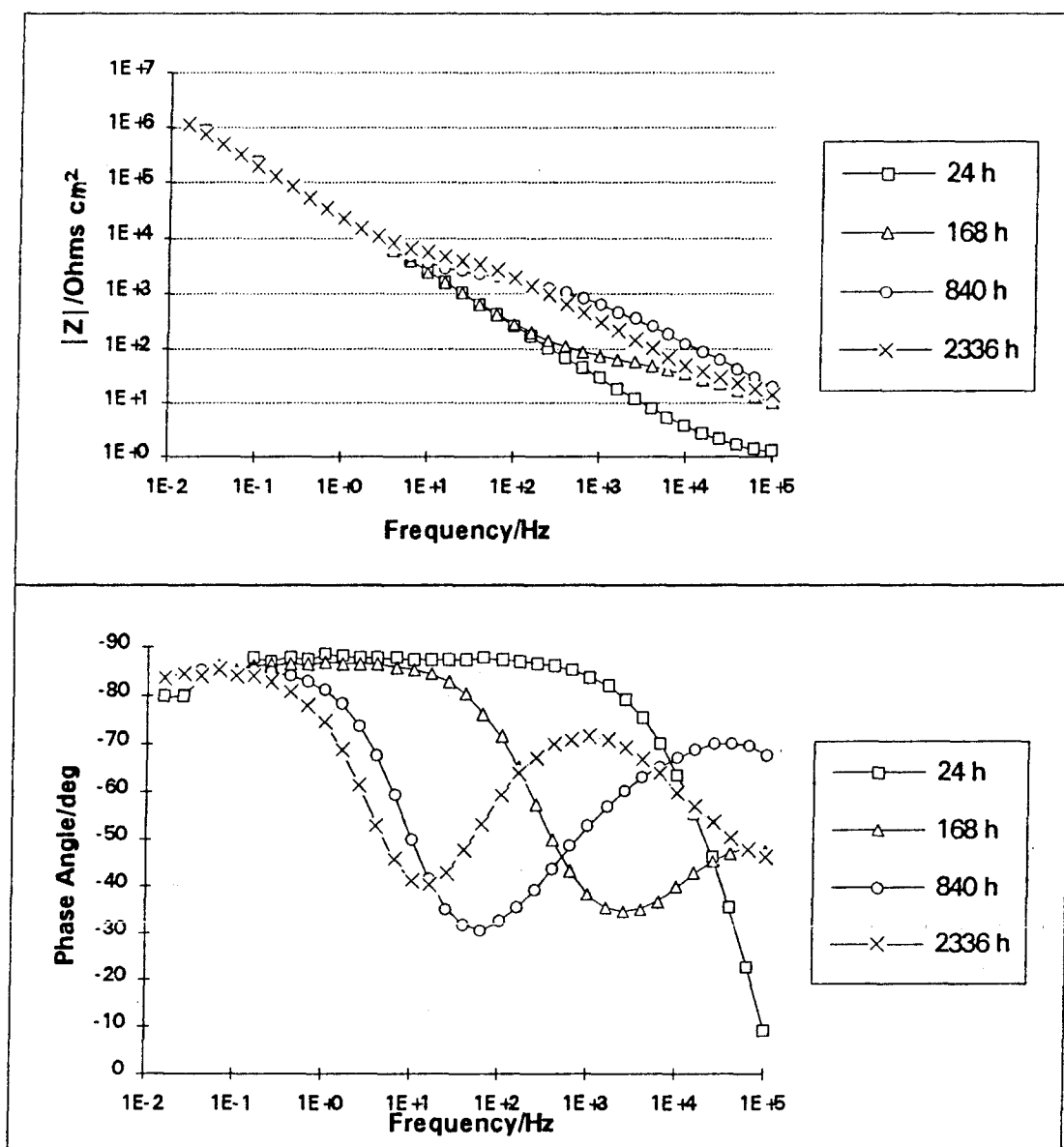


Figure 9. Bode plot of low coating-weight thin-film H_2SO_4 anodization on Al 7075 after 1 day, 8 days, 35 days, and 98 days immersion under electrolyte.

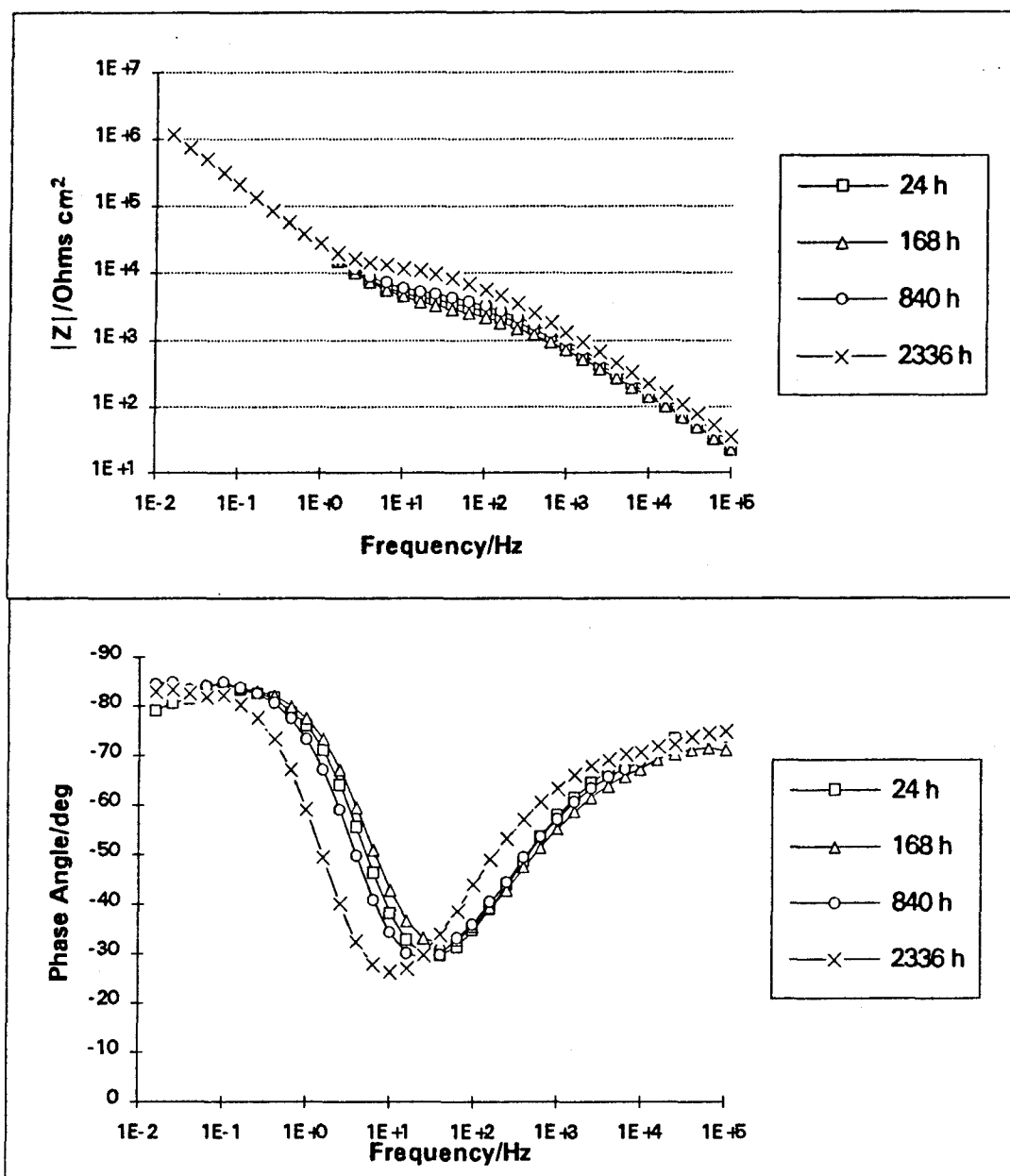


Figure 10. Bode plot of high coating-weight thin-film sulfuric-acid anodized 7075 Al at 1 day, 8 days, 35 days, and 98 days immersion under electrolyte.

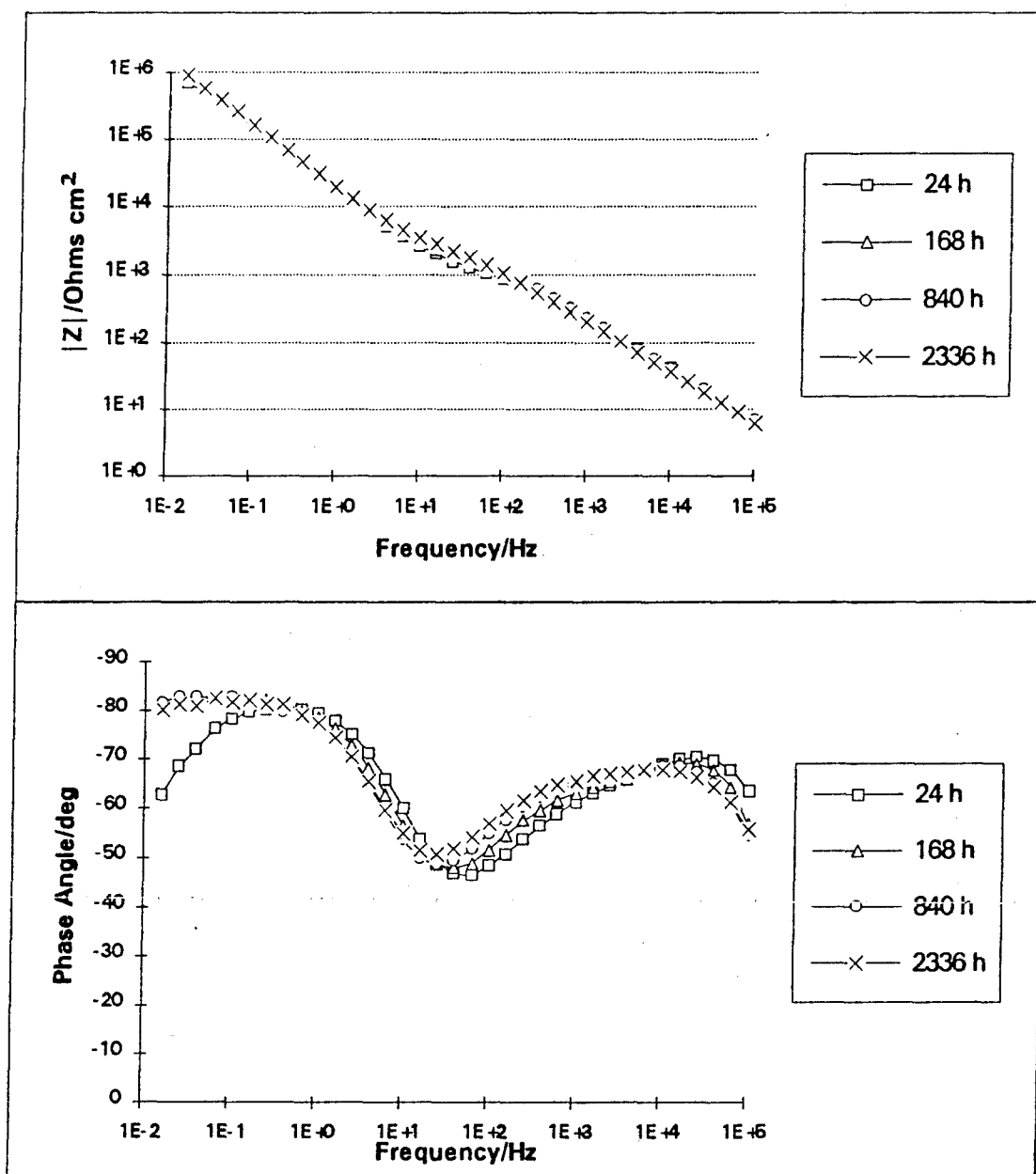


Figure 11. Bode plot of chromic-acid anodized 7075 Al at 1 day, 8 days, 35 days, and 98 days immersion under electrolyte.

In general, the thickness d_b of the barrier layer may be determined from the anodizing voltage, by the empirical factor $\sim 1.0 \text{ nm V}^{-1}$, under constant anodizing time.¹⁸ For freshly prepared, uncorroded samples, $d_b = 15 \text{ nm}$ for 7075 alloy and 17.5 nm for 2024 alloy for thin-film sulfuric acid (20 nm and 40 nm for the same alloys when chromic-acid anodized, respectively) is expected. Barrier thickness also may be found by measuring the capacitance C_b of the barrier layer. If we know the dielectric constant ϵ_b of the barrier material, then we can determine the thickness, which is inversely proportional to the capacitance, from the relation¹⁹

$$d_b = \frac{\epsilon_b \epsilon_0}{C_b}, \quad (2)$$

where $\epsilon_b \approx 10$, the dielectric constant of the barrier layer of anodic aluminum oxide²⁰; and $\epsilon_0 = 8.85 \times 10^{-14} \text{ A s cm}^{-2}$, the permittivity of a vacuum. From Table 8, Q_b may be substituted safely for C_b because α_b is nearly 1 for all panels, indicating a near-perfect capacitor. Using Equation 2, the calculated d_b for all panels after 1 day under salt solution was found to be 9 nm, in fair agreement with the d_b from anodizing voltage.

Table 8. Values of Porous and Barrier Circuit Components for Bare, Sealed Panels, after 1 Day Immersion in Electrolyte

Alloy	High Weight Thin-film H_2SO_4	Low Weight Thin-film H_2SO_4	Chromic-acid
7075	$R_p = 2.260 \times 10^4$ $Q_p = 2.724 \times 10^{-7}$ $\alpha_p = 0.8112$	$R_p = 13.11$ $Q_p = 2.981 \times 10^{-4}$ $\alpha_p = 0.5732$	$R_p = 8.206 \times 10^3$ $Q_p = 8.922 \times 10^{-7}$ $\alpha_p = 0.7766$
	$R_b = 7.730 \times 10^7$ $Q_b = 9.961 \times 10^{-7}$ $\alpha_b = 0.9485$	$R_b = 5.863 \times 10^7$ $Q_b = 9.551 \times 10^{-7}$ $\alpha_b = 0.9707$	$R_b = 1.490 \times 10^7$ $Q_b = 1.366 \times 10^{-6}$ $\alpha_b = 0.9218$
2024	$R_p = 7.518 \times 10^3$ $Q_p = 5.620 \times 10^{-7}$ $\alpha_p = 0.7675$	$R_p = 70.08$ $Q_p = 7.859 \times 10^{-6}$ $\alpha_p = 1.000$	$R_p = 5.895 \times 10^3$ $Q_p = 1.403 \times 10^{-6}$ $\alpha_p = 0.8062$
	$R_b = 3.515 \times 10^8$ $Q_b = 9.926 \times 10^{-7}$ $\alpha_b = 0.9513$	$R_b = 3.008 \times 10^7$ $Q_b = 9.714 \times 10^{-7}$ $\alpha_b = 0.9690$	$R_b = 7.571 \times 10^7$ $Q_b = 1.544 \times 10^{-6}$ $\alpha_b = 0.9368$

All resistances are in Ωcm^2 ; all constant-phase elements are in Fcm^{-2}

A general idea of the structural integrity of the porous film can be found by calculating its specific resistivity ρ_p from the equation¹⁹

$$R_p/d_p = \rho_p. \quad (3)$$

Table 9 shows specific resistivities for the various pretreatments. Note that the lowest thicknesses have ρ_p 100–1000 times smaller than the higher thicknesses, indicating penetration of electrolyte into the porous layer through serious flaws. The higher thicknesses have a ρ_p of $\sim 10^7 \Omega \cdot \text{cm}$, still a factor of 10 less than that found by Hitzig, *et al.*¹⁹ (whose porous layers were several times thicker than these panels, and whose sealing times were based on the parameter $3 \text{ min } \mu\text{m}^{-1}$). Hawkins, *et al.*, note that population densities of flaws are higher for thinner anodic layers.²¹

Table 9. Calculated Specific Resistivities for Porous Layers on Bare, Sealed Panels

Pretreatment	Alloy	$d_p/\mu\text{m}$	R_p/Ω	Calculated $\rho_p/\text{k}\Omega \cdot \text{cm}$
Thin-Film H_2SO_4	7075	2.67	13.1	49.1
		5.57	2.26×10^4	4.06×10^4
	2024	3.31	70.1	212
		7.58	7.52×10^3	9.92×10^3
Chromic-Acid	7075	4.22	8.21×10^3	1.94×10^4
	2024	4.88	5.90×10^3	1.21×10^4

The results in Tables 8 and 9 also suggest that the sealing method used in these experiments does not plug up the pores in the film, but, rather, "coats" them with oxide or dichromate, depending on the sealant solution. The relatively large values of Q_p (10^{-4} – $10^{-6} \text{ F} \cdot \text{cm}^{-2}$) for all panels as listed in Table 8 reveal an area exposed to electrolyte larger than that expected for completely plugged pores (10^{-8} – $10^{-9} \text{ F} \cdot \text{cm}^{-2}$).^{19,22,23} A larger Q means that the dielectric does not separate plates that are parallel; extra surface area (i.e., the walls of the pores) must be included in one plate of the capacitor.

Several graphs (Figures 12–14) show the evolution of the porous-layer circuit components, over the course of 98 days under electrolyte, for the different pretreatments and alloys. The least stable panels were the low-coating-weight thin-film sulfuric-acid anodized samples. On these panels, the initial porous resistance was quite low, as previously mentioned ($< 100 \Omega \cdot \text{cm}^2$), and increased in several weeks to an asymptotic limit of $\sim 10^4 \Omega \cdot \text{cm}^2$. This effect may be caused by gradual corrosion, oxide build-up, and plugging of thin spots and defects in the low-coating-weight pretreatment. Likewise, the porous capacitance dropped on these panels from $10^{-4} \text{ F} \cdot \text{cm}^{-2}$ to roughly 10^{-6} – $10^{-7} \text{ F} \cdot \text{cm}^{-2}$, indicating a thickening or plugging of the defective porous layer. The other panels were relatively stable, with the porous resistance remaining at $10^4 \Omega \cdot \text{cm}^2$ and the porous capacitance remaining near 10^{-6} – $10^{-7} \text{ F} \cdot \text{cm}^{-2}$ for the whole experiment. There was a gradual increase in the porous resistance with time, however. Such behavior was also observed by Mansfeld, *et al.* on hot-water-sealed ($\geq 30 \text{ min}$) Al 6061 panels anodized in sulfuric acid.²¹

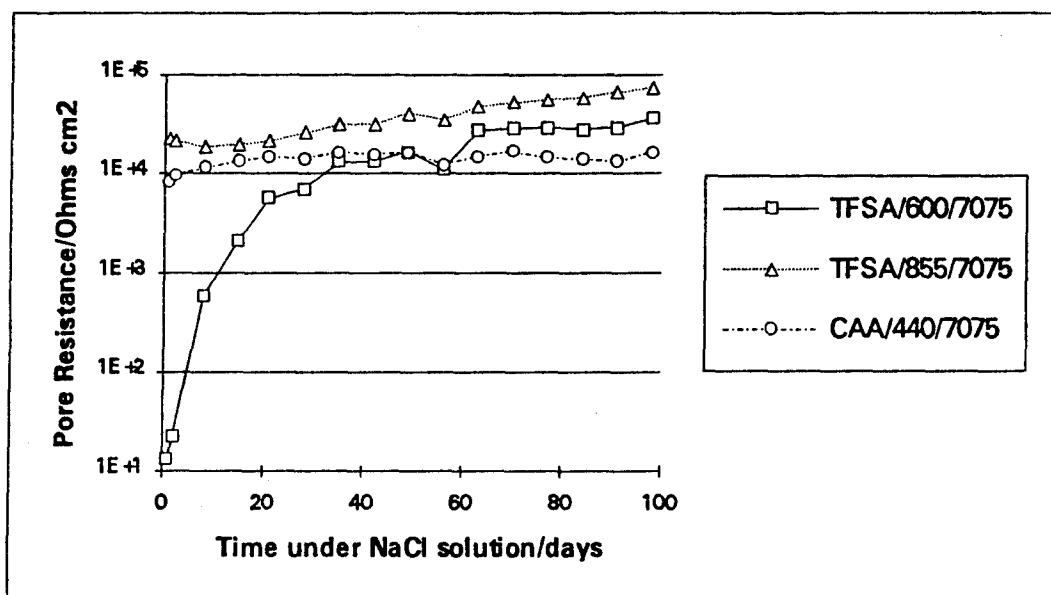


Figure 12. Porous resistance of bare, sealed panels vs time. Code is pretreatment/coating weight (mg ft⁻²)/alloy. TFSA = thin-film sulfuric-acid; CAA = chromic acid. Data for Al 2024 are not shown because they are similar to Al 7075, but with R_p about half that of Al 7075.

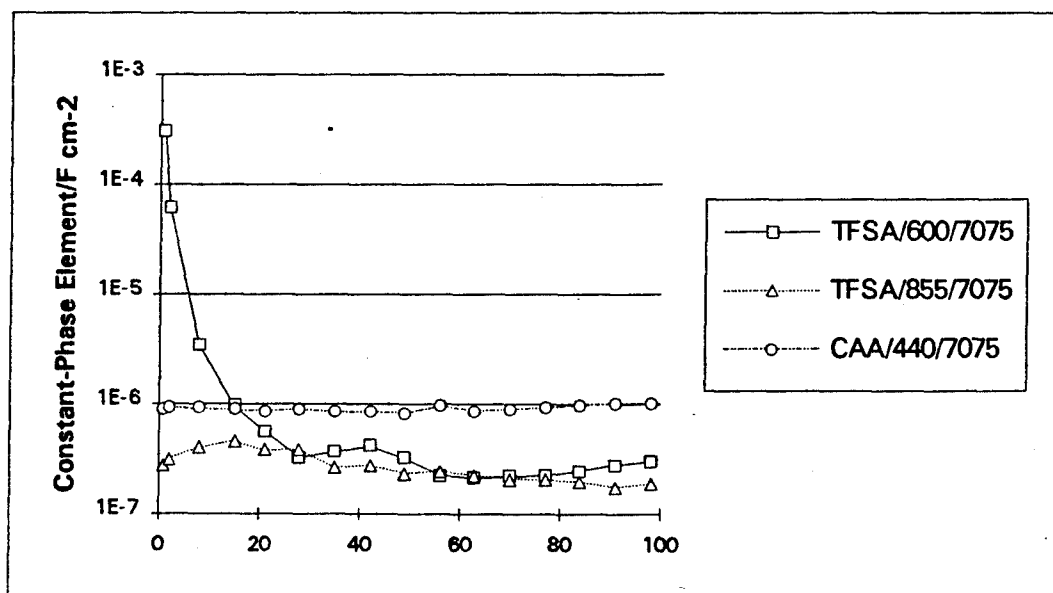


Figure 13. Porous constant-phase element of bare, sealed panels vs time. Code is pretreatment/coating weight (mg ft⁻²)/alloy. TFSA = thin-film sulfuric-acid; CAA = chromic acid. Data for Al 2024 are not shown because they are similar to Al 7075, but with Q_p about twice that of Al 7075.

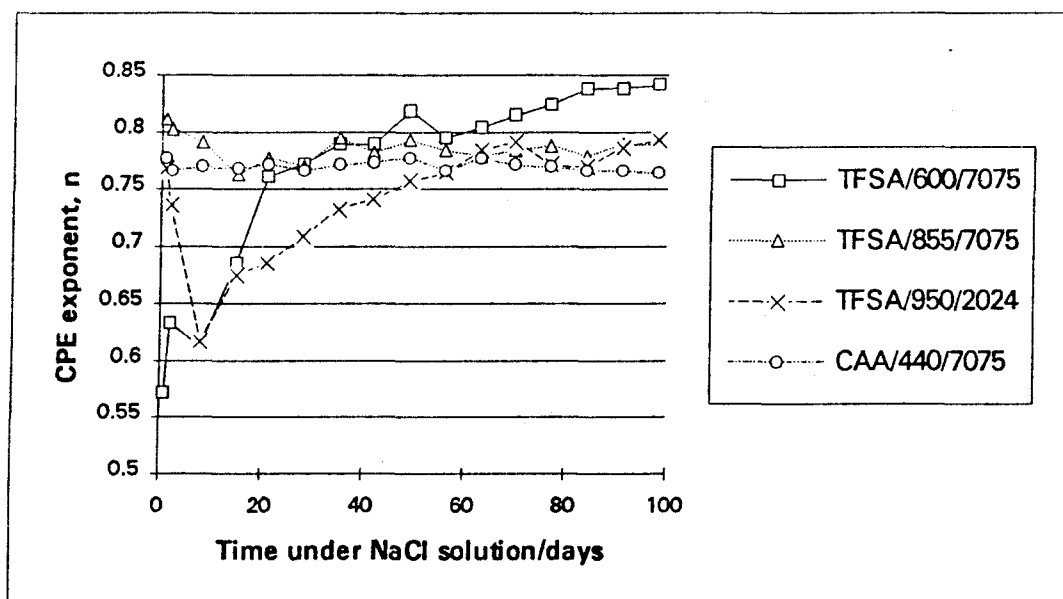


Figure 14. Porous constant-phase-element exponent of bare, sealed panels vs time. Code is pretreatment/coating weight (mg ft⁻²)/alloy. TFSA = thin-film sulfuric-acid; CAA = chromic acid. Data for TFSA/527/2024 and CAA/500/2024 are not shown because they are similar to Al 7075.

Notable, too, is the qualitative difference between the chromic-acid anodized panels and the thin-film sulfuric-acid anodized panels. Both chromic-acid anodized specimens exhibited a characteristic slight increase, then decrease of the porous resistance, and a concomitant slight linear increase in the porous capacitance. The thin-film sulfuric-acid anodized panels, however, exhibited only a monotonic increase in the porous resistance and decrease in porous capacitance. Chromic-acid anodized aluminum has only ~1% Cr in its barrier layer, while the residual amount of sulfate is substantially higher in sulfuric-acid anodized barrier layers.^{24,25} The co-ordination number of aluminum is only 6 in chromic-acid anodization, but is 4, 5, and 6 in sulfuric-acid anodization.²⁶ Residual anion content or the more amorphous structure of the barrier layer in sulfuric-acid anodization may be the cause of these differences in behavior.

A comparison of the effects of long-term neutral salt-spray exposure to EIS cells with NaCl electrolyte is seen by looking at Tables 10 and 11. After 98 d in an EIS cell, the porous resistances are all approximately $10^4 \Omega \cdot \text{cm}^2$ and the porous capacitances are all about $10^{-6} \text{ F} \cdot \text{cm}^{-2}$, indicating much less damage to the outer porous layer than for salt-spray exposure. The barrier layer resistances are all $\sim 10^8 \Omega \cdot \text{cm}^2$, indicating an undamaged barrier, unlike the salt-spray results. Such differences indicate that EIS results are less severe than, and not directly comparable to, long-term salt-spray tests.

Table 10. Values of Circuit Components for Bare, Sealed Panels,
after 3000 h in Neutral Salt-Spray

Alloy	High Weight Thin-film H_2SO_4	Low Weight Thin-film H_2SO_4	Chromic-acid
7075	$R_p = 8.526$ $Q_p = 5.596 \times 10^{-5}$ $\alpha_p = 0.6277$ $R_b = 1.188 \times 10^6$ $Q_b = 4.186 \times 10^{-6}$ $\alpha_b = 0.9191$	$R_p = 9.628$ $Q_p = 1.108 \times 10^{-4}$ $\alpha_p = 0.5209$ $R_b = 1.422 \times 10^5$ $Q_b = 1.606 \times 10^{-5}$ $\alpha_b = 0.9141$	$R_p = 61.17$ $Q_p = 2.388 \times 10^{-4}$ $\alpha_p = 0.3883$ $R_b = 2.468 \times 10^6$ $Q_b = 9.452 \times 10^{-6}$ $\alpha_b = 0.9393$
2024	$R_p = 57.36$ $Q_p = 3.491 \times 10^{-4}$ $\alpha_p = 0.5418$ $R_b = 2.272 \times 10^5$ $Q_b = 3.640 \times 10^{-5}$ $\alpha_b = 0.9123$	$R_p = 33.49$ $Q_p = 2.199 \times 10^{-4}$ $\alpha_p = 0.6449$ $R_b = 2.709 \times 10^5$ $Q_b = 3.678 \times 10^{-5}$ $\alpha_b = 0.8932$	$R_p = 188.4$ $Q_p = 8.246 \times 10^{-5}$ $\alpha_p = 0.6231$ $R_b = 1.643 \times 10^6$ $Q_b = 3.331 \times 10^{-5}$ $\alpha_b = 0.9073$

All resistances are in Ωcm^2 ; all constant-phase elements are in Fcm^{-2}

Table 11. Values of Circuit Components for Bare, Sealed Panels,
after 98 d Immersion in Electrolyte

Alloy	High Weight Thin-film H_2SO_4	Low Weight Thin-film H_2SO_4	Chromic-acid
7075	$R_p = 7.355 \times 10^4$ $Q_p = 1.863 \times 10^{-7}$ $\alpha_p = 0.7893$ $R_b = 1.804 \times 10^8$ $Q_b = 1.006 \times 10^{-6}$ $\alpha_b = 0.9533$	$R_p = 3.601 \times 10^4$ $Q_p = 2.790 \times 10^{-7}$ $\alpha_p = 0.8412$ $R_b = 2.323 \times 10^8$ $Q_b = 1.040 \times 10^{-6}$ $\alpha_b = 0.9563$	$R_p = 1.630 \times 10^4$ $Q_p = 1.014 \times 10^{-6}$ $\alpha_p = 0.7640$ $R_b = 1.208 \times 10^8$ $Q_b = 1.236 \times 10^{-6}$ $\alpha_b = 0.9253$
2024	$R_p = 1.650 \times 10^4$ $Q_p = 4.950 \times 10^{-7}$ $\alpha_p = 0.7929$ $R_b = 2.138 \times 10^8$ $Q_b = 1.168 \times 10^{-6}$ $\alpha_b = 0.9433$	$R_p = 5.753 \times 10^3$ $Q_p = 2.173 \times 10^{-6}$ $\alpha_p = 0.6519$ $R_b = 2.218 \times 10^8$ $Q_b = 1.131 \times 10^{-6}$ $\alpha_b = 0.9542$	$R_p = 6.868 \times 10^3$ $Q_p = 2.594 \times 10^{-6}$ $\alpha_p = 0.8011$ $R_b = 1.410 \times 10^8$ $Q_b = 1.655 \times 10^{-6}$ $\alpha_b = 0.9376$

All resistances are in Ωcm^2 ; all constant-phase elements are in Fcm^{-2}

Results for Painted Panels

A standard model with two time constants was found to be inadequate for modeling primed, unsealed, anodized aluminum panels. An attempt to use Kendig, *et al.*'s three-time-constant model²⁷ was also made, providing ambiguous results.²⁸ Instead, van Westing, *et al.*'s nested model (Figure 15) was employed with excellent results. (Grandle and Taylor recently used a similar model for coated aluminum cans.²⁹) Our interpretation of the model incorporates the usual solution resistance R_{sol} , coating capacitance Q_{pf} and resistance R_{pf} , pore capacitance Q_{pore} and resistance R_{pore} , charge transfer resistance R_{ct} with double-layer capacitance Q_{dl} , plus a pretreatment resistance R_{diff} and capacitance Q_{diff} . (All Q s represent constant-phase elements according to Equation 1.) This model not only includes an (RQ) term to describe the high porosity of this primer, but also has an (RQ) term for the underlying pretreatment. Figures 16–18 show Bode plots for the different pretreatments on unsealed panels painted with 23377 solvent-borne epoxy primer, at selected times of immersion under electrolyte. Bode plots for alloy 2024 again are not provided, because they reveal similarities to alloy 7075: low coating-weight H_2SO_4 on 2024 is similar to Fig. 17; high coating-weight H_2SO_4 on 2024 is similar to Fig. 16; and chromic-acid on 2024 is similar to Fig. 18.

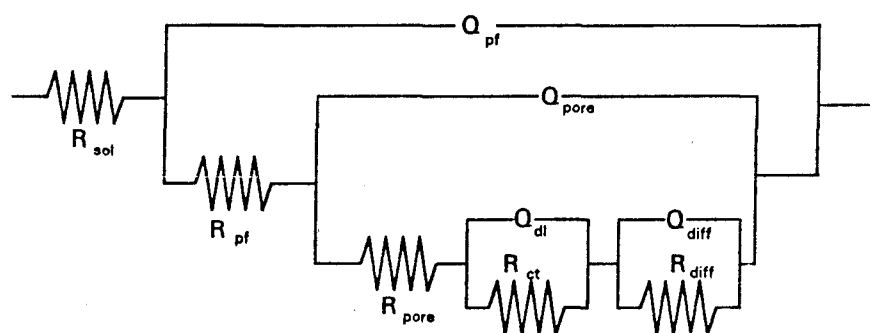


Figure 15. Equivalent circuit model for painted, unsealed panels.

The evolution of the different equivalent-circuit elements for primed panels with time is given in Figures 19–21. Again, plots for alloy 2024 are not provided because they appear similar to those for alloy 7075: low-weight thin-film H_2SO_4 on 2024 is similar to Fig. 20, high-weight thin-film H_2SO_4 is like Fig. 19, and chromic-acid on 2024 is similar to Fig. 21. Values for the pretreatment resistance R_{diff} are not given, for they are all $>10^8 \Omega \text{ cm}^2$.

All of the thin-film H_2SO_4 anodized panels exhibited an increase of charge-transfer resistance R_{ct} with a simultaneous drop in double-layer capacitance Q_{dl} . This indicated an initially high reaction rate across the paint-pretreatment interface that gradually slowed, with build-up of corrosion products. The chromic-acid anodized panels showed a early, rapid increase of R_{ct} (to $>10^9 \Omega \cdot \text{cm}^2$), presumably from corrosion inhibition by chromate, and then a decline to measurable levels

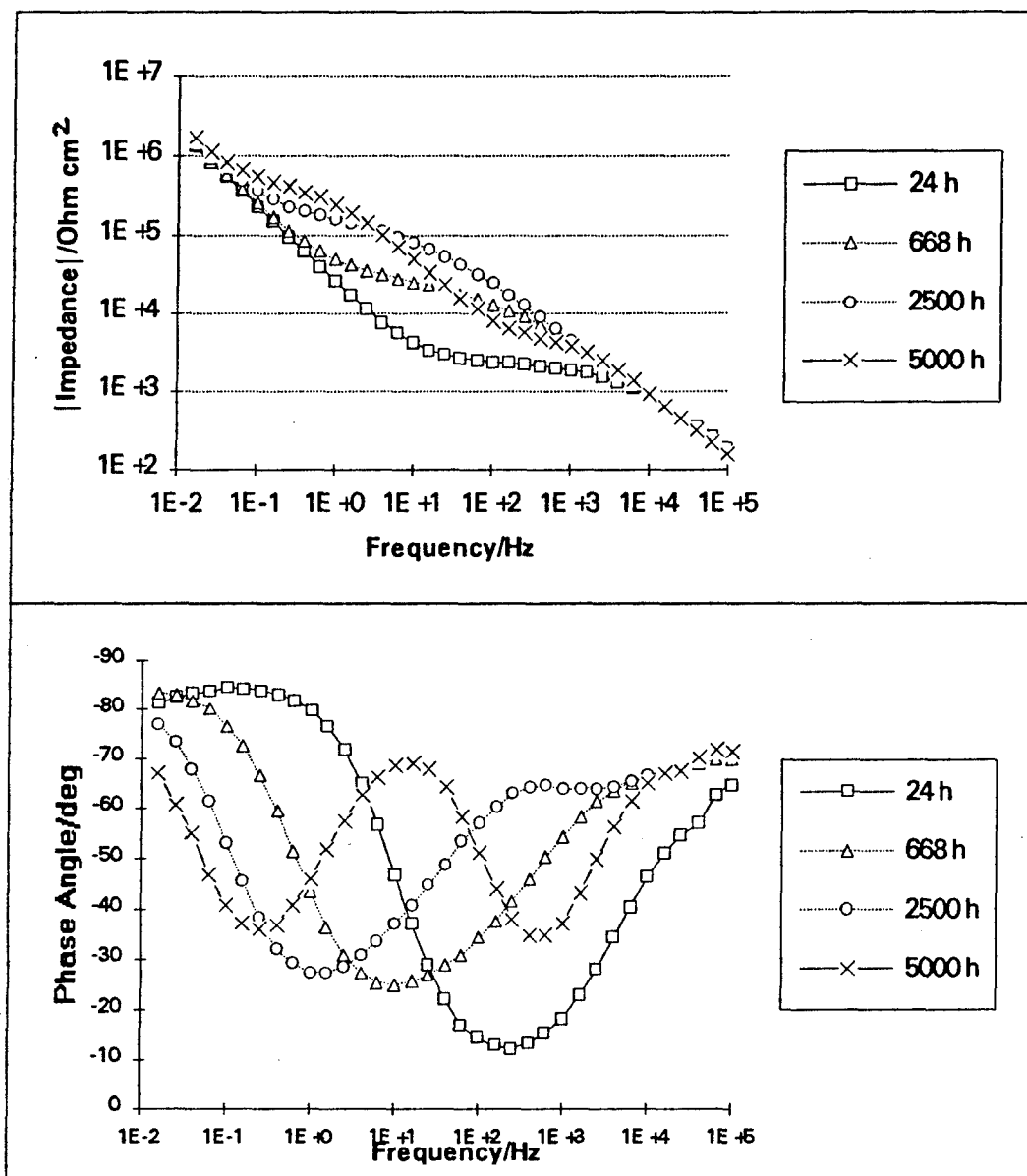


Figure 16. Bode plot of primed low coating-weight thin-film sulfuric-acid anodized 7075 Al after 1 day, 28 days, 105 days, and 210 days under electrolyte.

at later times. Under initial conditions, n_{pore} and n_{dl} were less than 1 for all systems, indicating extensive penetration of electrolyte into the interface.

Use of Equation 2 also shows the extensive uptake of water by the primer. In Table 12, thicknesses $d_{\text{permascope}}$ of the applied primer as measured by permascope are compared with those d_{pf} s as calculated using Eq. 2, from the coating capacitance Q_{pf} . Assuming that Q_{pf} is sufficiently close to a perfect capacitor C_{pf} (this assumption seems to be satisfied, for all fits indicate $n_{\text{pf}} >$

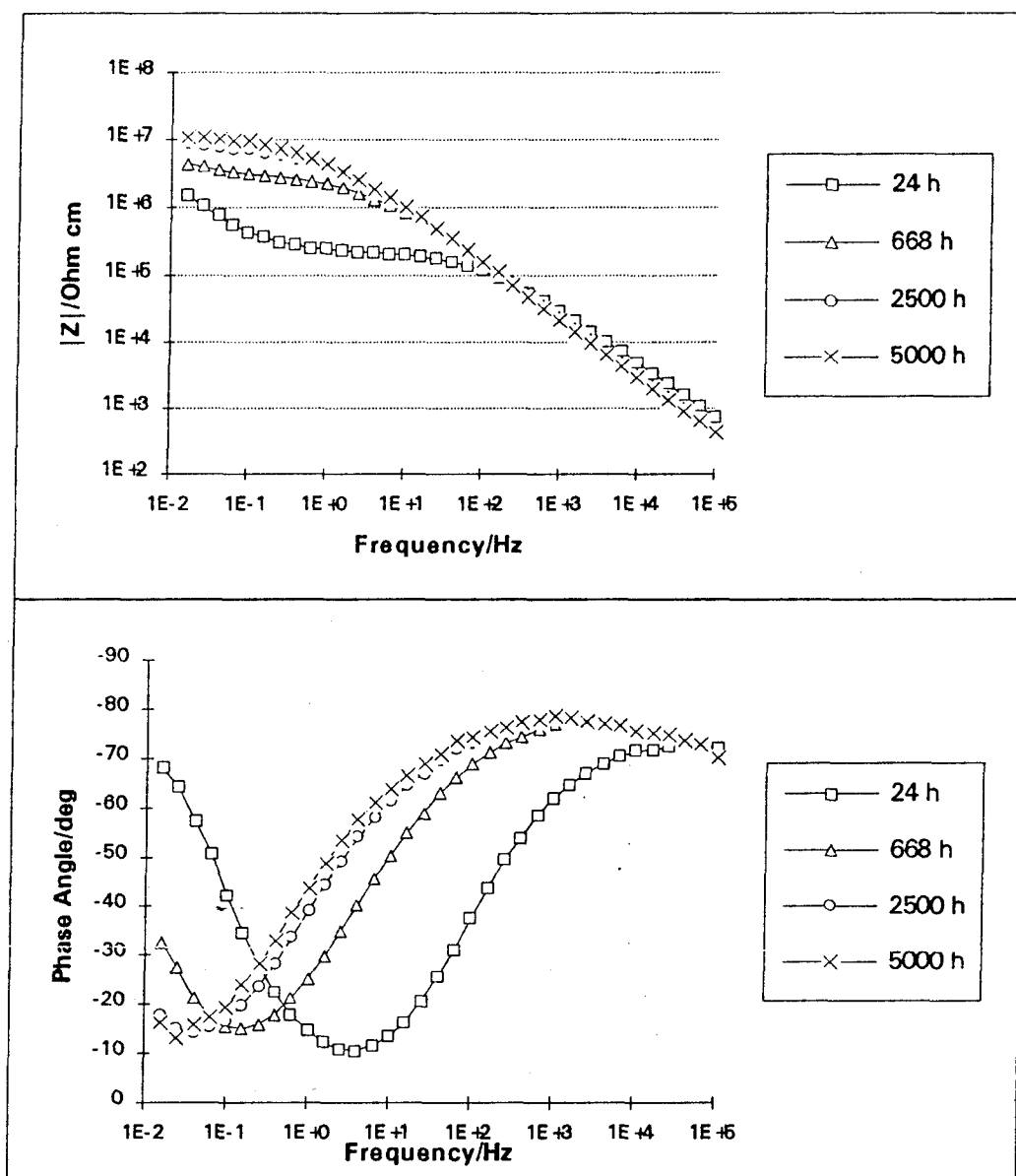


Figure 17. Bode plot of primed high-thickness thin-film H_2SO_4 anodization on Al 7075 after 1 day, 28 days, 105 days, and 210 days immersion under electrolyte.

0.9), a correlation was found between eventual number of blisters and pinholes and the measured initial primer ϵ , as shown in Table 12. Inspection of the panels' exposed area under $30\times$ magnification, after 210 days under the electrolyte, confirmed this belief: The high-weight thin-film sulfuric-acid anodized 2024 panel ($\epsilon = 72$) revealed numerous pinhole defects with bare Al visible; the low-weight thin-film sulfuric-acid anodized 7075 panel ($\epsilon = 28$) displayed many microscopic blisters; the other four panels showed little or no blistering, pinholes, or other defects. The ultimate tendency for high-porosity paint films will be towards the dielectric constant of water ($\epsilon = 79$)³⁰, because these films will absorb water the most rapidly. In contrast,

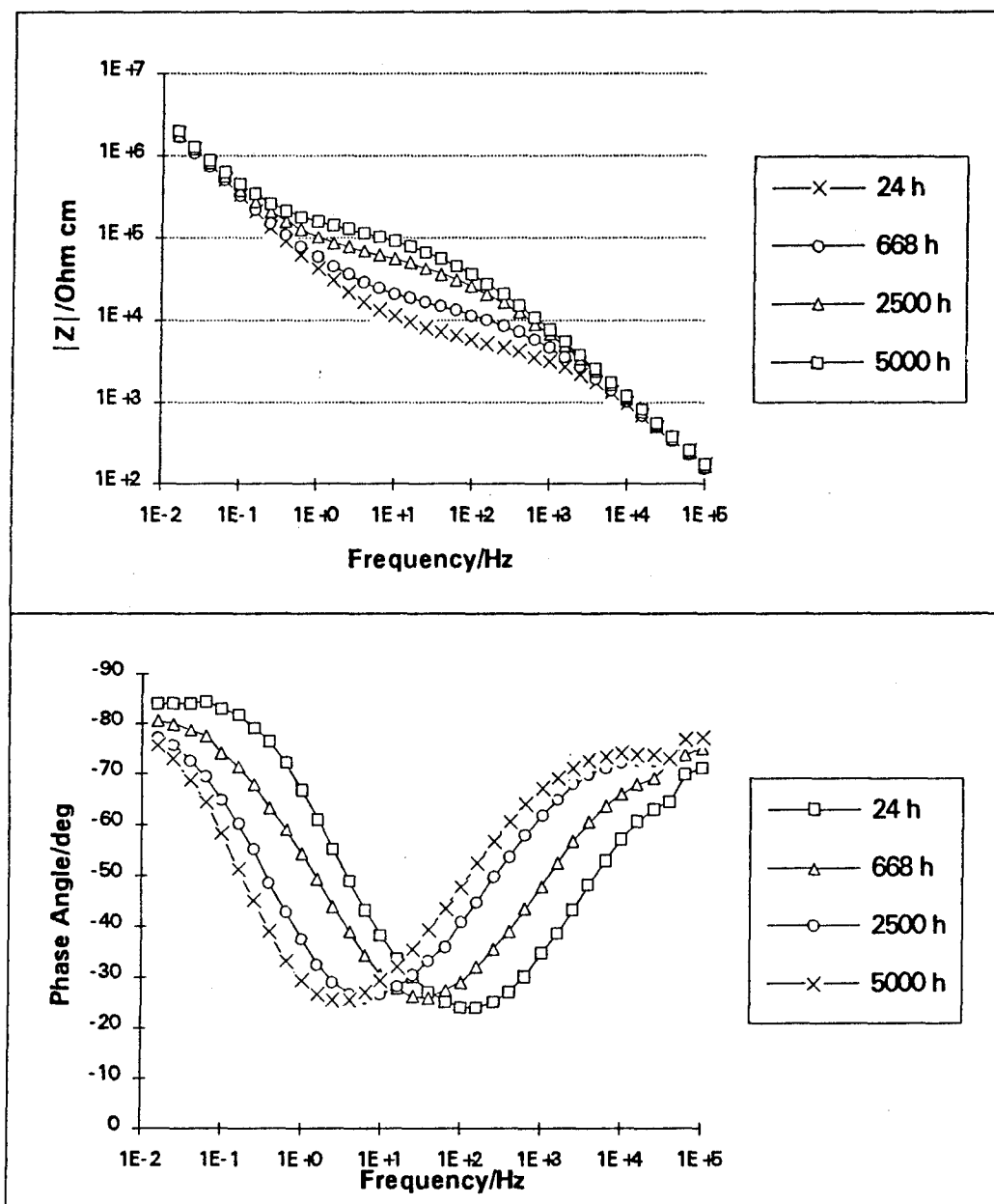


Figure 18. Bode plot of primed chromic-acid anodization on Al 7075 after 1 day, 28 days, 105 days, and 210 days immersion under electrolyte.

the least porous films will have a low initial dielectric constant, near that of epoxy resins ($\epsilon \approx 3.6$)³¹. This suggests that EIS may be a way of determining the overall relative quality of an applied epoxy paint film, by measuring ϵ within an hour of assembling an electrochemical cell. Clearly the primer, as applied, is not a barrier coating.

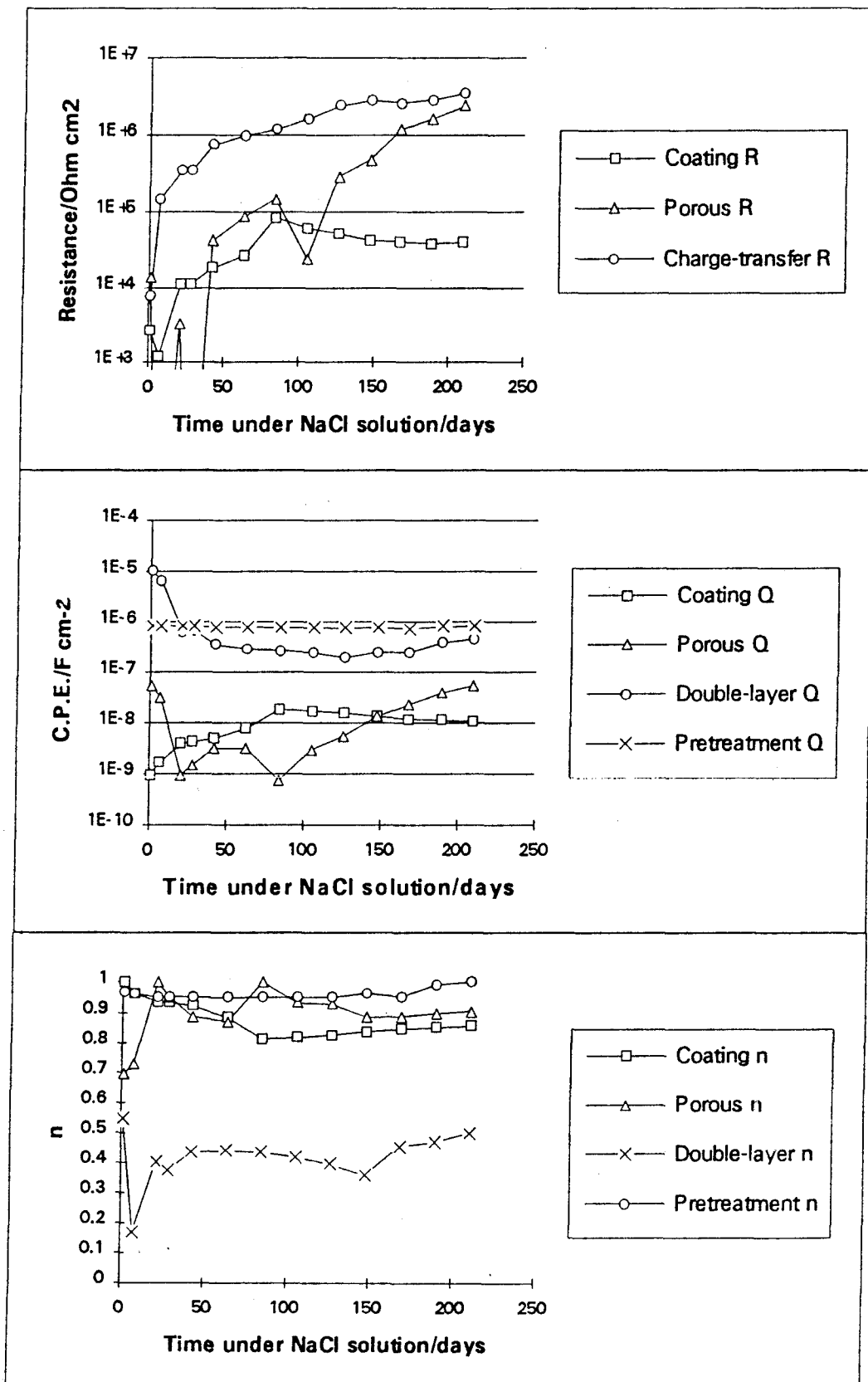


Figure 19. Evolution of circuit parameters with time for primed, low-weight H_2SO_4 anodization on Al 7075: (top) resistances, (middle) cpe's, (bottom) cpe exponents.

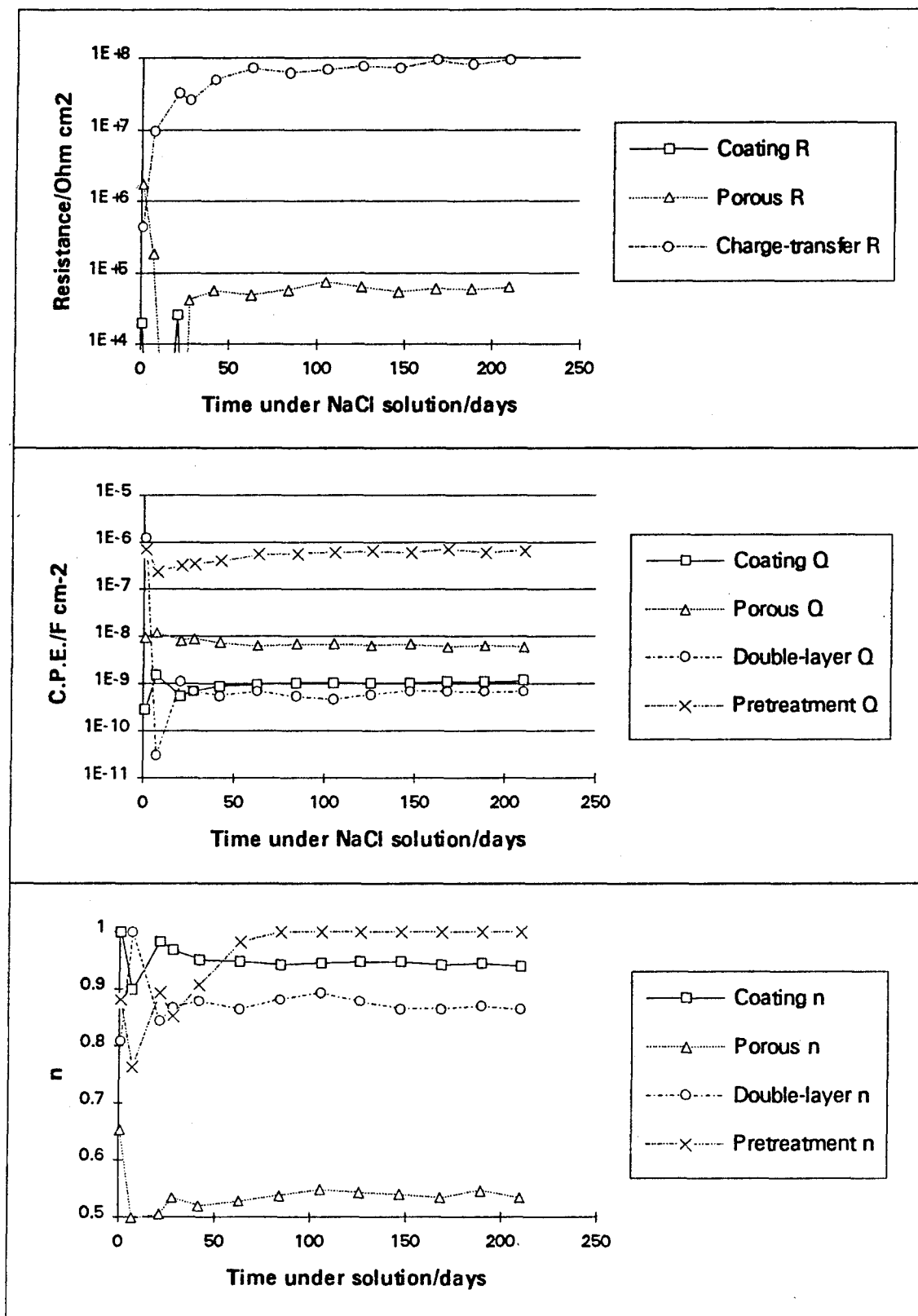


Figure 20. Evolution of circuit parameters with time for primed, high-weight H_2SO_4 anodization on Al 7075: (top) resistances, (middle) cpe's, (bottom) cpe exponents.

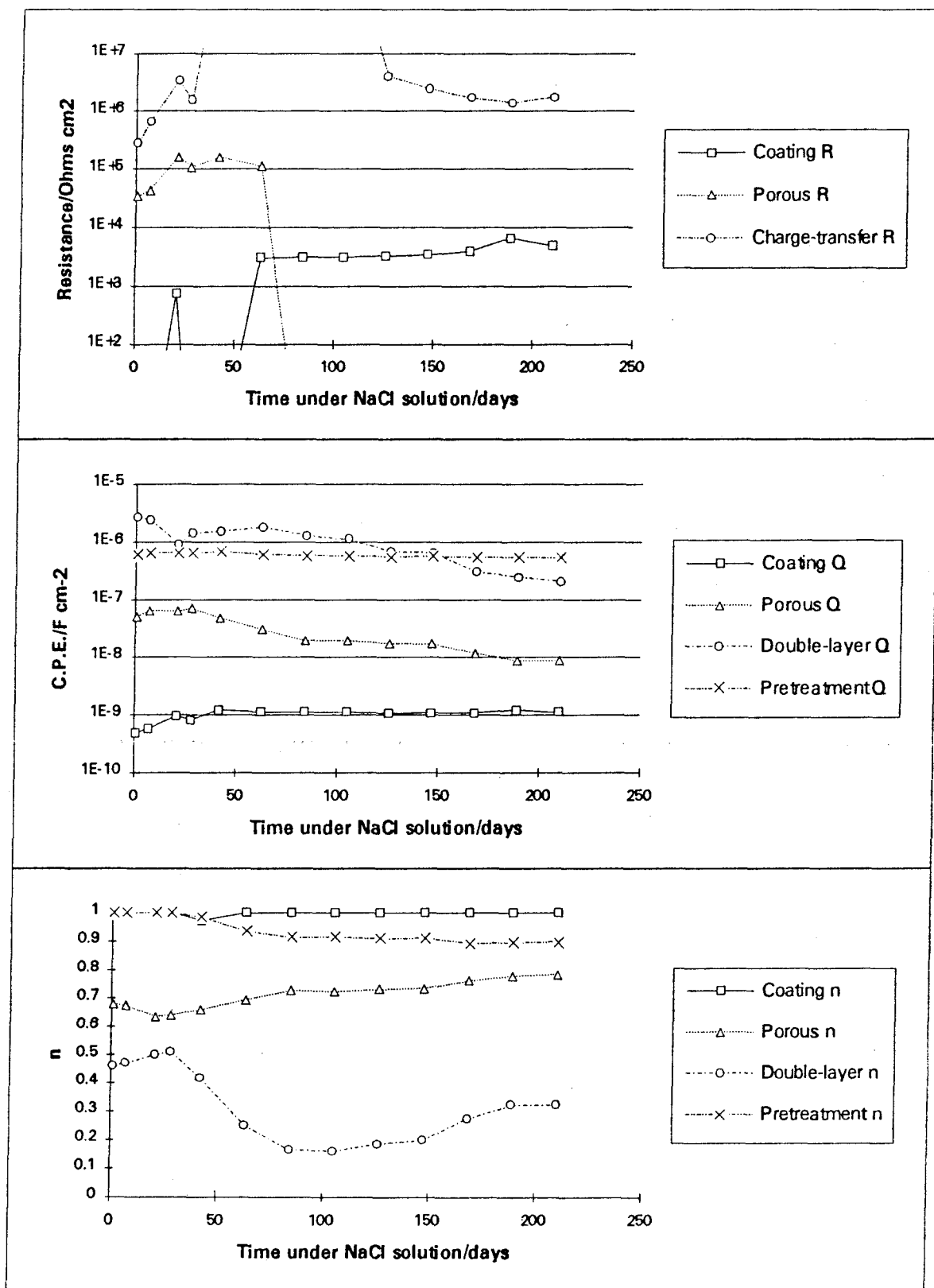


Figure 21. Evolution of circuit parameters with time for primed, chromic-acid anodization on Al 7075: (top) resistances, (middle) cpe's, (bottom) cpe exponents.

Table 12. Correlation between painted, pretreated panels' appearance and primer dielectric constant ϵ

Alloy, Pretreatment	Initial $Q_{pt}/nF\text{-cm}^{-2}$	Paint thickness/ μm	Calculated primer ϵ	Appearance after 210 d
7075, H_2SO_4 , low*	0.96	25.9 ± 1.3	28	some blisters
7075, H_2SO_4 , high*	0.28	34.5 ± 2.6	11	3 or 4 blisters
2024, H_2SO_4 , low*	0.33	35.8 ± 6.1	14	nothing
2024, H_2SO_4 , high*	1.7	37.8 ± 3.3	72	1 or 2 blisters; pinholes
7075, chromic-acid	0.57	$19. \pm 2$	12	nothing
2024, chromic-acid	0.74	$22. \pm 1$	18	nothing

*Low designates low coating weight, and *high* indicates high coating weight. Measured after 24 h.

Error in paint thickness is one σ derived from 10 measurements per panel.

Summary

The current military specification for type IIC coating lists acceptable coating weights between 200 and 1000 mg ft^{-2} . According to the results presented herein, coating weights below approximately 600 mg ft^{-2} provide inadequate protection, especially on 7075 aluminum. The porous layer created at such low coating weights seems to be full of defects. Chromate, an active corrosion inhibitor, can protect such flaws in the chromic-acid anodized samples against attack, but chromate is not present at high enough levels in thin-film sulfuric-acid anodized aluminum when sealed in dichromate solution. Above this level of coating weight, however, thin-film sulfuric-acid anodized panels give acceptable protection, provided an adequate primer is applied. The current minimum coating weight for thin-film sulfuric-acid anodization ought to be raised to at least 600 mg ft^{-2} , and painted panels must be sealed first, to improve paint adhesion.

Acknowledgement

The authors would like to express their appreciation to Mr. William J. Green, Mr. Donald J. Hirst, Mr. Frank R. Pepe, and Dr. Kevin J. Kovalski for technical assistance. Special thanks are due to Dr. Herbert Stark for many discussions concerning analysis and interpretation of electrochemical impedance data.

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